

PTO 11-0353

CC=EP  
DATE=20020313  
KIND=A2  
PN=1186581

NITROGEN-FREE SUBSTANCE FOR USE AS FERTILIZER  
[STICKSTOFFFREIER STOFF ZUR VERWENDUNG ALS DUENGEMITTEL]

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UNITED STATES PATENT AND TRADEMARK OFFICE  
WASHINGTON, D.C. NOVEMBER 2010  
TRANSLATED BY: SCHREIBER TRANSLATIONS, INC.

|                               |        |                                                                   |
|-------------------------------|--------|-------------------------------------------------------------------|
| PUBLICATION COUNTRY           | (10):  | EP                                                                |
| DOCUMENT NUMBER               | (11):  | 1186581                                                           |
| DOCUMENT KIND                 | (12):  | A2                                                                |
| PUBLICATION DATE              | (43):  | 20020313                                                          |
| APPLICATION NUMBER            | (21):  | 01121819.5                                                        |
| APPLICATION DATE              | (22):  | 20010911                                                          |
| INTERNATIONAL CLASSIFICATION  | (51):  | C05D 9/00                                                         |
| PRIORITY COUNTRY              | (33):  | AT                                                                |
| PRIORITY NUMBER               | (31):  | 6702000                                                           |
| PRIORITY DATE                 | (32):  | 20000912                                                          |
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| DESIGNATED CONTRACTING STATES | (84):  | AT BE CH CY DE DK ES FI FR<br>GB GR IE IT LI LU MC NL PT<br>SE TR |
| TITLE                         | (54):  | NITROGEN-FREE SUBSTANCE FOR<br>USE AS FERTILIZER                  |
| FOREIGN TITLE                 | [54A]: | STICKSTOFFFREIER STOFF ZUR<br>VERWENDUNG ALS DUENGEMITTEL         |

**Description**

[0001] The invention concerns a nitrogen-free substance for use as spreadable fertilizer, soil additive, culture substrate, or growth stimulator containing 50 to 90% by weight of stone dust consisting preferably of a mixture of different stone minerals, 5 to 50% by weight of 3-layer minerals, 1 to 25% by weight of zeolite, as well as 1 to 5% by weight of bonding agents, in particular dextrin, and nitrogen-bonding bacteria. The invention additionally concerns a process for producing such a nitrogen-free substance.

[0002] The use of fertilizers, soil additives, culture substrates or growth stimulators in agriculture ensures a high productivity and quality assurance, and it is therefore no longer conceivable to eliminate it from this branch of the economic system from an economic point of view.

[0003] It is known, on the other hand, however, that the massive use of fertilizers during the last few centuries has lead to a deterioration of the soil, which was first countered by further increasing the supply of fertilizers. The consequence was the destruction of the ecological balance of the soil and an erosion of the mineral substances contained in the soil, as well as an endangerment of the underground water above all due to nitrates.

**[0004]** It is therefore a need and object of the invention to reduce the nitrogen supply through fertilizers in order to reduce the nitrogen burden and still ensure that useful plants are supplied with nitrogen, so that the growth-enhancing effect of the main and trace nutrients on useful plants does not have to be relinquished.

**[0005]** The object is attained in that the initially described substance contains in addition 0.1 to 10% by weight of a dry admixed sulfate mixture comprising magnesium, sodium, copper, manganese, zinc and/or iron sulfate.

**[0006]** Stone dust, preferably consisting of a mixture of different very finely ground stone minerals in a proportion of 50 to 90% by weight, 3-layer clay minerals in a proportion of 5 to 50% by weight, zeolite in a proportion of 1 to 25% by weight, as well as bonding agents, in particular dextrin with added water in a proportion of 0.1 to 10% by weight, and nitrogen-bonding bacteria are mixed in order to produce a nitrogen-free substance according to the invention for use as spreadable fertilizer, soil additive, culture substrate, or growth stimulator. A sulfate mixture comprising magnesium, sodium, copper, manganese, zinc and/or iron sulfate is then dry added in a proportion of 0.1 to 10% by weight.

[0007] The pH value is changed toward neutral by admixing sulfates. The sulfur contained in the sulfate is offered as a fast and evaporation-proof component available as nutrient.

[0008] The formation of an ionic equilibrium is prevented by means of the dry admixture of sulfate compounds and the different admixed sulfate compounds act separately on the plant in direct connection and proportion with respect to each other, depending on their element order. The absorption depends again directly from the intensity of the light source (solar irradiation). When the substance is used as fertilizer, for example, the fertilizer amount can be reduced by up to 40% with respect to the conventionally used amount without a diminution of the fertilizing effect.

[0009] This dry mixture also promotes the antagonism-synergism effect and an overreaction (overfertilization of a single nutrient) cannot take place therefore in the plants or the accumulation of an individual element is made difficult. The effect of the individual nutrients is retained as a result of the dry admixture. The plant can freely select which nutrients will be absorbed and it can be determined that the water stress (drought) during periods of prolonged drought no longer has such great importance (the wither protection starts later) and dry periods are thus better withstood by the plants.

[0010] Sulfate further reduces the water content by forming hydration water, which has a positive effect on the shelf life.

[0011] The substance according to the invention mobilizes the nutrient reserves (for example, phosphorous, potassium, trace elements) existing in the soil and contains furthermore important main and trace elements in a form available for plants. The substance strengthens the plant tissue due to its high silicic acid content (silicon). The substance improves the soil structure and boosts the soil fauna.

[0012] The substance increases the vitality of the plant components. The cell walls develop stronger, so that the applied amounts of fungicides and growth regulators can be clearly reduced or in part also omitted. The maintenance liming can likewise be saved at the same time with the application of the substance.

[0013] The sulfates increase the efficiency of the substance and accelerate the provision of different nutrients in the soil nutrient budget.

[0014] The substance is preferably available as a granulate on which the nitrogen-bonding bacteria are sprayed with a nutrient solution preferably consisting of acetates and molybdate.

[0015] The granulate is dried and sifted after granulation via a Peltier plate. Spraying of the nitrogen-bonding bacteria (acetobacter) with the nutrient solution

preferably consisting of acetates and molybdate, takes place immediately after sifting.

[0016] The granulate is applied as soil fertilizer. The granulate can be spread with any fertilizer spreader due to its granularity.

[0017] A granulate with the following amount ratios is produced for testing purposes. 25% of dolomite, 25% of biotite (half pH-neutral or acid basalt), 40% of clay compounds (expanded clay 15%, 25% of illite-vermiculite mixture, wherein the mixture of illite and vermiculite can consist of 5-54% of illite and 10-81.7% vermiculite) and 4% of quartz-free zeolite (clinoptilolite - natural zeolite) were mixed with 2% of dextrin as bonding agent (obtained from starch of agriculturally useful plants) and 1% of water. 3% of sulfates were dry admixed.

[0018] The nutrient content was as follows:

| Main Nutrient:                |                        | Trace Nutrients: |
|-------------------------------|------------------------|------------------|
| SiO <sub>2</sub>              | 30.00% of Silicic Acid | Iron             |
| CaO                           | 16.20% of Calcium      | Manganese        |
| MgO                           | 9.40% of Magnesium     | Zinc             |
| K <sub>2</sub> O              | 0.41% of Potassium     | Copper           |
| P <sub>2</sub> O <sub>5</sub> | 0.19% of Phosphate     | Boron            |
|                               |                        | Molybdenum       |
|                               |                        | Cobalt           |
|                               |                        | Selenium         |

[0019] A granulate produced therefrom was sprayed with a solution containing nitrogen-bonding bacteria (azotobacter) and

used as test fertilizer for the cultivation of numerous agricultural cultures. Sugar water enriched with Mg, Na, Fe, Cu, Zn, Mn and Mo, which had previously been solubilized with acetic acid (acetate), was used as nutrient solution of bacteria (azotobacter - azotobacteraceae strains). The nitrogen-bonding bacteria were added for propagation at a temperature of approx. 25°C into this nutrient solution. The liquid was diluted by approx. two thirds with water after a few days with good propagation and was used to spray onto the granulate. Good effects on the fruit quality and yielded amount and an improvement of the soil quality were noticed.

**[0020]** The admixture of sulfates has allowed attaining an extremely fast and very efficient increase in effectiveness of the granulate, which can be visibly noticed very fast a short time after application through the increased growth activity as well as the darker green of the leaves. It was possible to immensely improve the short and long term effect as a result of this composition according to the invention.

#### **Patent Claims**

1. A nitrogen-free substance for use as spreadable fertilizer, soil additive, culture substrate, or growth stimulator containing 50 to 90% by weight of stone dust, preferably a mixture of different stone minerals, 5 to 50% by weight of 3-layer clay minerals, 1 to 25% by weight of zeolite, as



well as 1 to 5% by weight of bonding agents, in particular dextrin, and nitrogen-bonding bacteria, **characterized in that** the substance also contains 0.1 to 10% by weight of a dry admixed sulfate mixture, which comprises magnesium, sodium, copper, manganese, zinc and/or iron sulfate.

2. The substance of Claim 1, **characterized in that** the substance is available as a granulate, on which the nitrogen-bonding bacteria are sprayed with a nutrient solution, which preferably consists of acetates and molybdate.
3. A process for the production of a nitrogen-free substance for use as spreadable fertilizer, soil additive, culture substrate, or growth stimulator in which stone dust, consisting preferably of a mixture of different stone materials in a proportion of 50 to 90% is mixed with 3-layer clay materials in a proportion of 5 to 50% by weight, zeolite in a proportion of 1 to 25% by weight, as well as bonding agents, in particular dextrin, in a proportion of 1 to 5% by weight and nitrogen-bonding bacteria, **characterized in that** a sulfate mixture comprising magnesium, sodium, copper, manganese, zinc and/or iron sulfate is dry admixed to this mixture in a proportion of 0.1 to 10% by weight.

4. The process of Claim 3, **characterized in that** the substance is granulated, dried, and then sprayed with a nutrient solution containing nitrogen-bonding

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bacteria, which preferably consists of acetates and molybdate.

PTO 11-0352

CC=DE  
DATE=19960111  
KIND=A1  
PN=19523334

FERTILIZER GRANULATE WITH NITROGEN-BINDING BACTERIA  
[DÜNGEMITTELGRANULAT MIT STICKSTOFFBINDENDEN BAKTERIEN]

ROBERT KARNER

UNITED STATES PATENT AND TRADEMARK OFFICE  
WASHINGTON, D.C. NOVEMBER 2010  
TRANSLATED BY: SCHREIBER TRANSLATIONS, INC.

|                               |        |                                                             |
|-------------------------------|--------|-------------------------------------------------------------|
| PUBLICATION COUNTRY           | (10):  |                                                             |
| DOCUMENT NUMBER               | (11):  | 19523334                                                    |
| DOCUMENT KIND                 | (12):  | A1                                                          |
| PUBLICATION DATE              | (43):  | 19960111                                                    |
| APPLICATION NUMBER            | (21):  | 19523334.4                                                  |
| APPLICATION DATE              | (22):  | 19950627                                                    |
| INTERNATIONAL CLASSIFICATION  | (51):  | C05C 11/00<br>C05G 1/00                                     |
| PRIORITY COUNTRY              | (33):  | AT                                                          |
| PRIORITY NUMBER               | (31):  | 16094                                                       |
| PRIORITY DATE                 | (32):  | 19940407                                                    |
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| APPLICANT(S)                  | (71):  | ROBERT KARNER                                               |
| DESIGNATED CONTRACTING STATES | (81):  | N/A                                                         |
| TITLE                         | (54):  | FERTILIZER GRANULATE<br>WITH NITROGEN-BINDING<br>BACTERIA   |
| FOREIGN TITLE                 | [54A]: | DÜNGEMITTELGRANULAT MIT<br>STICKSTOFFBINDENDEN<br>BAKTERIEN |

## Specification

The invention relates to a substance used as fertilizer, soil amendment, cultivation substrate, or farming auxiliary.

The use of such substances in agriculture provides for high productivity and quality assurance, and is therefore no longer to be ignored economically from this branch of the economy.

On the other hand, however, it is well known that the massive use of fertilizers in recent decades has led to damage to the soil, which was treated at first by the further addition of fertilizers. The result was destruction of the ecological balance of the soil and leaching of the minerals contained in the soil, as well as endangerment of groundwater, especially by nitrates.

It is therefore necessary, and the purpose of the present invention, to reduce the introduction of nitrogen through fertilizers in order to lower the nitrate load and nevertheless to provide for a nitrogen supply to the commercial plants, so as not to have to do without the growth-promoting effect of nitrogen on commercial plants.

This goal is reached by providing that a substance used as fertilizer, soil amendment, cultivation substrate, or farming auxiliary contains nitrogen-binding bacteria.

Such nitrogen-binding bacteria are naturally present in inherently healthy soil and bring the nitrogen in a form available to plants. In case of damaged soil or intensive utilization, however, not enough nitrogen-binding bacteria are present in the soil and the nitrogen introduced by fertilizers cannot be stored to be taken up by the plants when needed, but is leached out of the soil in the form of nitrate. By providing a nitrogen-binding bacterium with the substance pursuant to the invention, the plant excretes sugars, carbohydrates, etc., when nitrogen is needed, which nourish the nitrogen-binding bacteria which in turn return nitrogen to the plant; thus no leaching can occur. If the soil is over-fertilized, the nitrogen can be sharply reduced even to zero, since the bacteria supplied with the substance (granulate) pursuant to the invention make the nutrients present in the soil available to the plants, with the soil being cleansed at the same time.

The substance is preferably a granulate that carries the nitrogen-binding bacteria on its surface. In this form the substance can be easily introduced into the soil and provides for immediate efficacy of the bacteria in their nitrogen-binding function.

Azospirillum, Azotobacter, and/or Azotobacteraceae are preferably used as nitrogen-binding bacteria.

The substance pursuant to the invention can also contain dextrin as binder and bacterial nutrients, which assures good adhesion and an adequate number of bacteria.

The invention also relates to a method for producing a substance used as fertilizer, soil amendment, cultivation substrate, or farming auxiliary as described above, with a solution containing nitrogen-binding bacteria being sprayed onto the granulate and with the granulate then being subjected to a drying process.

Specifically, a nutrient solution with nitrogen-binding bacterial was applied in trials to a conventional granulate, as described below:

The granulate consisting of various finely ground rock minerals (approx. 2/3 by weight) and 3-layer clay minerals (approx. 1/3 by weight), and a small proportion of magnesium oxide. An additional 2% of dextrin was admixed as binders for this granulate. After blending, granulation is carried out by adding water (pelletizing). This granulate is fed through a vibrating dryer where the granulate is heated by about 200°C. It is then cooled and subsequently screened. The granulate at this time had a temperature of about 40°C.

After screening, a nutrient solution was sprayed onto the granulate with the nitrogen-binding bacteria. This nutrient

solution consists of sugar water supplemented with the following nutrients:

Magnesium, sodium, iron, copper, zinc, manganese, and strengthened molybdenum that was previously broken down with acetic acid (acetate). The nitrogen-binding bacteria were added to this nutrient solution at a temperature of about 25°C to multiply. After a few days with good multiplication, the liquid was diluted by about two-thirds water and was used for spraying onto the granulate.

After applying to the granulate and from its still-elevated temperature, further multiplication of the nitrogen-binding bacteria occurred. Stabilization of the nitrogen-binding bacteria until it was applied was provided for by the dextrin in the granulate.

The granulate prepared in this way was used in trials to fertilize farm growth all agricultural crops and showed good effects on fruit quality, quantity produced, and improvement of soil quality.

#### Patent Claims

1. Substance used as fertilizer, soil amendment, cultivation substrate, or farming auxiliary, **characterized in that** nitrogen-binding bacteria are included.



2. Substance pursuant to Claim 1, characterized in that the substance is a granulate that carries the nitrogen-binding bacteria on its surface.

3. Substance pursuant to Claim 1 or 2, characterized in that *Azospirillum*, *Azotobacter*, or *Azotobacteraceae* are used as nitrogen-binding bacteria.

4. Substance pursuant to one of the preceding claims, characterized in that dextrin is also included as a bacterial nutrient.

5. Method for producing a substance used as fertilizer, soil amendment, cultivation substrate, or farming auxiliary pursuant to one of the claims 1 to 4, characterized in that a solution containing nitrogen-binding bacteria is sprayed onto the granulate.

PTO 11-0144

CC=SU  
DATE=19820623  
KIND=A1  
PN=937436

METHOD OF PRODUCING NITROGEN-CONTAINING FERTILIZER WITH  
MICROELEMENTS  
[SPOSOB POLUCHENIYA AZOTOSODERZHASHCHEGO UDOBRENIYA S  
MIKROELEMENTAMI]

A. YE. KUZNETSOVA, ET AL.

UNITED STATES PATENT AND TRADEMARK OFFICE  
WASHINGTON, D.C.                      OCTOBER, 2010  
TRANSLATED BY: SCHREIBER TRANSLATIONS, INC.

|                               |        |                                                                                |
|-------------------------------|--------|--------------------------------------------------------------------------------|
| PUBLICATION COUNTRY           | (10):  |                                                                                |
| DOCUMENT NUMBER               | (11):  | 937436                                                                         |
| DOCUMENT KIND                 | (12):  | A1                                                                             |
| PUBLICATION DATE              | (43):  | 19820623                                                                       |
| APPLICATION NUMBER            | (21):  | 290180                                                                         |
| APPLICATION DATE              | (22):  | 19800129                                                                       |
| INTERNATIONAL CLASSIFICATION  | (51):  | C 05 C 9/02                                                                    |
| PRIORITY COUNTRY              | (33):  | N/A                                                                            |
| PRIORITY NUMBER               | (31):  | N/A                                                                            |
| PRIORITY DATE                 | (32):  | N/A                                                                            |
| INVENTOR(S)                   | (72):  | A. YE. KUZNETSOVA, ET<br>AL.                                                   |
| APPLICANT(S)                  | (71):  | N/A                                                                            |
| DESIGNATED CONTRACTING STATES | (81):  | N/A                                                                            |
| TITLE                         | (54):  | METHOD OF PRODUCING<br>NITROGEN-CONTAINING<br>FERTILIZER WITH<br>MICROELEMENTS |
| FOREIGN TITLE                 | [54A]: | SPOSOB POLUCHENIYA<br>AZOTOSODERZHASHCHEGO<br>UDOBRENIYA S<br>MIKROELEMENTAMI  |

(54) Method of Producing Nitrogen-Containing Fertilizer with  
Microelements

The invention pertains to methods of producing nitrogen-containing fertilizer with microelements.

A method of producing complex granulated fertilizers is known, which includes preparation of a urea-formaldehyde solution by dissolving crystalline urea in formaldehyde at 40-45°C.

Salts of the microelements  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{ZnSO}_4$ ,  $\text{MnSO}_4$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{H}_3\text{BO}_3$  are dissolved in an aqueous solution of thiourea. The resulting solution, which contains the complex compound of a microelement with thiourea, is added to a mixture of phosphoric acid and potassium chloride while stirring; next this mixture is placed in a urea-formaldehyde solution [1].

The disadvantage of this method is the fact that scarce salts are used as the source of the microelements.

The solution closest to the invention technically and to the achieved result, is a method of producing urea granules coated with microelements, according to which one mixes finely ground water-soluble salts of a microelement (Fe, Mn, Mo, Cu, Zn, Cl) with urea granules. They are made to interact in dry form, as a result of which urea granules are formed that are coated

with an amount of salt in the range of 0.01-10% that is not toxic for plants. Then it is dried at 20-100°C and under pressure below 100 ml Hg. The resulting coating contains microelements and prevents caking of the urea granules [2].

However, the derived granules of urea do not cake only in the early stages of storage, but after one month of storage the

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granules do cake, because the coating of the urea granules is hygroscopic and during storage absorbs moisture. The stability of the granules is 0.5/granule. Moreover, the urea granules are quickly dissolved by the irrigation and subsoil moisture, and therefore the nitrogen and microelement utilization factors by plants are insignificant, comprising 40-50%.

The aim of the invention is to increase the utilization factor of nitrogen and microelements and to improve the strength of the granules.

This goal is reached by the method of producing a nitrogen-containing fertilizer with microelements by applying microelements to the surface of the granules; as the source of the microelements one uses a mixture of sulfide ores and prior to application of the microelements the granules are additionally treated with an aqueous suspension of Thiobacillus ferrooxidans.

In this case the mixture of sulfide ores contains chalcopyrite and zinc blende in the ratio of minerals 1.8-2:1.

In addition, the entire coating comprises 2.3-4.5% of the weight of fertilizers.

Bacteria are introduced in the amount of 5-15% of the weight of sulfide ores in the form of 1.6-4.7% aqueous suspension.

Example 1: 1400 g of a complex polymer fertilizer based on urea, formaldehyde and ammophos, which contains 28% N, 22%  $P_2O_5$ , is fed to a fluidized bed reactor, where in the first stage of the fertilizer is sprayed using a spray nozzle with an aqueous suspension of *Thiobacillus ferrooxidans* bacteria in the amount of 1.6 g (approximately 5% of the ore weight) in 100 ml of water.

Next, in the second stage, a powdery mixture of ores is blown into the moistened fertilizer in the fluidized bed reactor; the mixture of ores moves uniformly with the fertilizer and nitrogen-containing fertilizer with microelements and sticks to it. For this purpose one takes 31.5 g of sulfide ore powder following flotation, which contains 21 g of 95%  $CuFeS_2$  (approximately 0.5% Cu of the fertilizer weight) and 10.5 g of 95%  $ZnS$  (approximately 0.5% Zn of the fertilizer weight). Mixing is carried out with air at 25-30°C, and the fertilizer is dried at the same time. As a result one gets a stratified fertilizer: The internal core is fertilizer, next a thin layer

of bacteria and layer of ore powder. The resulting product contains, %: N 27.8, Cu 0.5,  $P_2O_5$  21.7, and Zn 0.5.

Breakdown of the sulfide ores with the formation of dissolved salts of the microelements occurs by a biological process in the soil, because the strains of *Thiobacillus ferrooxidans* microorganisms produce free sulfuric acid during their vital activity.

The sulfuric acid breaks down the  $CuFeS_2$  and  $ZnS$  with the release of dissolved sulfate salts of copper and zinc.

Example 2: 1400 g of a complex polymer fertilizer, which contains 28% N and 22%  $P_2O_5$  is fed to a fluidized bed reactor, where in the first stage by means of a spray nozzle it is sprayed with an aqueous suspension of *Thiobacillus ferrooxidans* bacteria in the amount of 4.7 g (approximately 15% of the ore weight) in 100 ml of water.

Next, in the second stage, 31.5 g of a powdery mixture of ores (after flotation) is blown into the moistened fertilizers in the fluidized bed reactor; the ore mixture contains 21 g of  $CuFeS_2$  (0.5% Cu, of the fertilizer weight) and 10.5 g of  $ZnS$  (0.5% of the fertilizer weight). Mixing occurs with air at 25-30°C. Simultaneously the fertilizer is dried. The resulting product contains, %: N 27.8; Cu 0.5;  $P_2O_5$  21.7; Zn 0.5

Example 3: 1400 g of nitroammophoska, which contains 16% N, 16%  $P_2O_5$ , 18%  $K_2$ ), is fed to the fluidized bed reactor, where in the first stage by means of a spray nozzle an aqueous suspension of *Thiobacillus ferrooxidans* is sprayed in the amount of 3 g (approximately 5% of the ore weight) in 100 ml of water.

Then, in the second stage, to the moistened fertilizer in the fluidized bed reactor one blows in 63 g of a powdery ore, picked up after flotation, which contains 42 g of  $CuFeS_2$  (1% Cu of the fertilizer weight) and 21 g of  $ZnS$  (1% Zn of the fertilizer weight). Mixing occurs with air at 25–30°C. The resulting product contains, %: N 15.8; Cu 1;  $P_2O_5$  15.7; Zn 1;  $K_2O$  17.3.

Example 4: 1400 g of a complex polymer fertilizer based on urea, formaldehyde and ammophos, which contains 28% N, 22%  $P_2O_5$ ,

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is fed to the fluidized bed reactor, where in the first stage of the fertilizer is sprayed with an aqueous suspension of *Thiobacillus ferrooxidans* bacteria by means of a spray nozzle in the amount of 3.6 g (approximately 12% of the ore weight) in 100 ml of water.

Next, in the second stage, one blows toward the moistened fertilizer in the fluidized bed reactor, a powdery mixture of ores, which uniformly mixes with the fertilizer and sticks to it. To accomplish this one takes 29.50 g of sulfide ore powder



following flotation, which contains 19 g of 95%  $\text{CuFeS}_2$  and 10.5 g of 95%  $\text{ZnS}$ . Intermixing is carried out with air at 25-30°C, and the fertilizer is dried at the same time. The resulting product contains, %: N 27.8;  $\text{P}_2\text{O}_5$  21.7; Cu 0.45; Zn 0.5.

The fertilizer produced is dust-free, dark gray in color, and does not cake during storage. The coating of the granules is uniform, and it firmly adheres to the fertilizer surface due to the *Thiobacillus ferrooxidans* bacterial biomass glue.

The stability of the granules is 0.8 kg/granule.

This process of producing fertilizer is technically simpler in comparison with the existing one because it does not require special drying, and coating of the granules occurs in a fluidized bed. Breakdown of the sulfide ores with formation of microelement salts occurs biologically in the ground. It is known that biological breakdown occurs slowly; therefore the plants will assimilate microelements, and also nitrogen and phosphorus of the fertilizers during the entire growing period. According to agrochemical test data the utilization factors of nitrogen, phosphorus and microelements reaches 75-80%.

#### CLAIMS

1. A method of producing nitrogen-containing fertilizer with microelements by applying the latter to the surface of

granules characterized in that in order to increase the utilization factor of nitrogen and microelements and to improve the stability of the granules, a mixture of sulfide ores is used as the source of the microelements, and prior to application of the microelements the granules are additionally treated with an aqueous suspension of *Thiobacillus ferrooxidans*.

2. Method according to Claim 1 characterized in that the mixture of sulfide ores contains chalcopyrite and zinc blende in the ratio of minerals 1.8-2.1.
3. Method according to Claim 1 characterized in that the entire coating is 2.3-4.5% of the fertilizer weight.
4. Method according to Claim 1 characterized in that the bacteria are added in the amount of 5-15% of the weight of sulfide ores in the form of 1.6-4.7% aqueous suspension.

Information sources considered by the examining board:

1. USSR Author's Certificate No. 422710, Cl C 05 C 9/02, 1971.
2. USA Patent No. 3,617,239, Cl. 71-28, 1971 (original).